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The Aluminum Smelting Process

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This introduction to the industrial primary aluminum production process presents a short description of the electrolytic reduction technology, the history of aluminum, and the importance of this metal and its production process to modern society. Aluminum's special qualities have enabled advances in technologies coupled with energy and cost savings. Aircraft capabilities have been greatly enhanced, and increases in size and capacity are made possible by advances in aluminum technology. The metal's flexibility for shaping and extruding has led to architectural advances in energy-saving building construction. The high strength-to-weight ratio has meant a substantial reduction in energy consumption for trucks and other vehicles. The aluminum industry is therefore a pivotal one for ecological sustainability and strategic for technological development.

A luminum (Al) is a raw material of sustainability in the built environment, technology, and the modern economy. The ease with which aluminum can be resmelted, without losing durability or modifying its original properties, allowed it to become a high-value recycled commodity, serving as a cornerstone for the recycling industry. This property, but also its lightweight and in particular its structural strength, gives aluminum a unique role in building the structures and infrastructure of sustainable communities. The properties of the metal enable ecologically efficient services: transporting people further and faster with lower energy inputs; bringing power to new, growing, productive communities with fewer energy losses; and building green cities. Its advantages for sustainability and low maintenance have resulted in increasing use in modern construction, particularly in fast-growing economies.

The production and use of aluminum metal is a modern phenomenon. Gold and lead were smelted over 8000 years ago, and the Bronze Age of copper, tin, and zinc began over 6000 years ago. Silver was late to be separated, over 4000 years ago. Iron, which requires much higher temperatures, only became available about 3000 years ago. Aluminum has only been refined for about 200 years. Before about 1850, it was more valuable than gold because refining it was so difficult

Despite this, more aluminum is produced today than all other nonferrous metals combined. The total annual world production of primary aluminum was about 50 million metric tonnes in 2013, and in addition around 20 million tonnes was recycled. One billion tonnes of aluminum has been produced in history, and 800,000 tonnes since 1980. Around 75% of all the aluminum ever produced is still in productive use, reflecting not only the metal's recyclability, its long life, and durability, but also the significant growth in demand in recent years.

Production of primary aluminum involves two independent energy-intensive processes to transform the ore, which is bauxite, to the metal by electrolytic reduction. These are the Bayer process, which makes alumina from bauxite, using thermochemical digestion,

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and the Hall-Héroult process, which produces molten aluminum by electrolytic reduction of alumina dissolved in a molten fluoride electrolyte consisting mainly of cryolite. Cryolite is a mineral consisting of fluoride, sodium, and aluminum, Na₃AlF₆, which is the solvent for alumina in the smelting process. (Cryolite also exists in a natural form as a rare mineral, found almost exclusively in Greenland, but the mines were exhausted several decades ago.)

To support the Hall-Héroult process, carbon anodes have to be produced and this step involves carbon and carbonaceous compounds, which contribute most of the historical greenhouse gas emissions and occupational cancer risk associated in the past with the Hall-Héroult process. In the past, fluoride pollution, caused by hydrogen fluoride formation and vaporization from the electrolyte, was a very serious problem around aluminum smelters. Nevertheless, all aluminum producers now have highly efficient alumina dry scrubbing equipment, which removes up to 99% of all fluoride emissions from the cells. This is one of the success stories of modern aluminum production.

In 1856 the French chemist Henri Etienne Sainte-Claire Deville (1818 to 1881) succeeded in producing aluminum by electrolysis of molten sodium aluminum tetrachloride, NaAlCl₄. In the period up to 1890, about 200 metric tonnes of aluminum was produced by Deville's method.

Nevertheless, during that period, another and much more efficient process was invented. In 1886, Charles Martin Hall in the United States found that aluminum oxide (alumina, Al_2O_3) would melt at a temperature much lower than $2050^{\circ}C$ if it were first mixed with this rare mineral known as cryolite. He surmised that if he passed electric current through this molten mixture of alumina and cryolite, he could produce aluminum metal, and on February 23, 1886, aluminum was electrolyzed from alumina for the first time.

Coincidentally, Paul Louis Toussaint Héroult in France had also produced pure aluminum with $\mathrm{Al_2O_3}$ together with cryolite, and on April 23, 1886, he received a French patent on the process. These two men worked completely independently of each other, but their patents were very similar. The only difference, a very minor one, was that the carbon anodes in Héroult's process were larger and less numerous than in Hall's technique.

These two men, Hall and Héroult, were both born in 1863, and independently invented the aluminum production process in the same year, 1886, at the age of 23 years. Completing the remarkable coincidences, both died in 1914, at the age of 51 years. They met each other only once, in 1911.

The timing of the breakthrough, however, was anything but arbitrary or coincidental. By the late 1880s, large dynamos had been developed and the technology had been refined for over a decade to the point where they were newly capable of supplying the high electric currents required for the electrolytic process. A year later the Austrian chemist Karl Josef Bayer (1847 to 1904) invented an improved method for producing alumina from bauxite more efficiently on a large scale, for which he was issued a patent in 1887. The so-called Bayer process greatly boosted yield and practicality of the Hall and Héroult method.

Since 1886, the industrial aluminum production has developed from art to science. A steadily increased understanding of the process has been achieved because of extensive research and development work, particularly in the latter half of the twentieth century, both in aluminum plants and in several universities and academic institutions.

The principal technological change was in preparation of the carbon anode from petroleum coke and pitch. The anode is slowly consumed in the electrolysis process, under intense heat, and releases greenhouse gas emissions, particularly carbon dioxide, and polycyclic aromatic hydrocarbons in the so-called Søderberg process. There an anode is continually formed by adding briquettes of petroleum coke and pitch to the top of the anode, where it "bakes" in place. The Søderberg process has been almost universally replaced by the "prebake" system, in which the anode is made outside the cell, baked in a so-called anode baking furnace at high temperature at another location, where emissions are easier to capture and control. It is then transported and placed into the electrolytic cell for operation. The prebake system results in much lower emissions of harmful polycyclic aromatic hydrocarbons in general, once installed in the cell.

Today, most aluminum smelters of the "prebake" anode technology are very similar, and differ mostly in cell amperage and the number of cells. The building housing the cell lines is called the "potroom." This building may be more than 1 km long, in some cases about 50 m wide and perhaps 20 m high. Inside, there are hundreds of aluminum electrolysis cells and each of them can be 10 to 15 m long. A photograph of a modern cell line is shown in Fig. 1.

Production of liquid aluminum is continuous inside the cells. Day and night each of the cells produces this valuable metal at amounts of 100 kg or more every hour. The largest aluminum smelters in the world now have production capacities in excess of 1 million tonnes per year.

There is often very little difference in cell design from smelter to smelter. The tops of the anode rods extend above the many aluminum hoods that cover the cell. The hoods facilitate collection of the cell gases and particulates for treatment in the gas cleaning plant. Large vertical aluminum bars (called anode risers) conduct the current from the negative cathode of the neighbor cell to the positive anode of the next cell. Within the cell, the anodes are dipped into the electrolyte and covered, and the cathode part of the cell is located in the basement under the floor of the building.

In the aluminum industry, the size of the cells is not measured in meters, but in kiloamperes (kA). Large cells are now about 300 kA or higher, whereas small cells have amperages below 200 kA. The world's largest cells at present are 600 kA.

Inside one of these cells, there is a crusty layer of alumina and solid electrolyte, mostly cryolite, on top of the anodes. There are usually some open holes in the crust along the center line between



FIGURE 1. A modern aluminum cell line showing high-amperage side-by-side prebake electrolysis cells.

the two rows of anodes, where the alumina is added automatically to the electrolyte. Underneath the crust, there is a deep layer of 15 to 20 cm of molten electrolyte and then a deep layer of 10 to 20 cm of molten aluminum. They separate because these two materials have different densities and do not mix. Alumina is dissolved in this electrolyte as ions, and aluminum is then produced at the negative cathode.

Temperatures in the potroom buildings are high because of the heat emitted from the cells, and there is often some alumina dust in the air. Strong static magnetic fields are caused by the large electric current, sufficient to stop watches, demagnetize credit cards, and disrupt pacemakers, which are not permitted in the potroom.

Cells are prone to disruptive current surges called "anode effects," which occur when the alumina concentration in the electrolyte becomes too low for sustainable cell operation. Then the electrical resistance in the cell abruptly increases because of the formation of an insulating gas layer that sits on the underside of the anodes. When these occur, unwanted greenhouse gas emissions (perfluorocarbons, CF_4 , and C_2F_6) from the anode are formed. Anode effects are quenched by a quick shorting of the current and then by adding more alumina.

Operating a smelter is not an easy task, requiring careful attention to minimize the frequency of occasional upset conditions and to keep cell operation within set parameters. During monitoring and intervention in the process, cell operators are constantly faced with decision-making situations. Theoretical and practical training for the operators and their supervisors and superintendents have developed the skills and knowledge needed to steadily improve cell operation and work practices. This, in turn, has led to more efficient and cost-effective production of aluminum. Cell operation has become a specialized occupation with skills that accrue to all stakeholders including local communities.

At any given time, there may be no operators at all working in the potroom. The whole area may look deserted. At other times, operational work will be performed in a well-rehearsed sequence proceeding down the rows of cells, as the process is far from being fully automated. Cranes move back and forth for transportation and changing of anodes and for removal of aluminum from the cells. Large vehicles transport the molten metal out of the building to the nearby cast house, for further metal treatment and casting of solid aluminum products.

In many vehicles in many smelters, operators are completely enclosed with climate control. Working in the potroom, standard personal protective equipment includes a hard hat, safety glasses, a fire-retardant coat, hearing protection, and safety shoes, and in some cases a respirator will be required.

The world's aluminum industry is now facing two major technological challenges: meeting or reducing the high electrical energy requirements; and mitigating environment impacts during production processes, including emissions from power generation before delivery to the potroom. The solutions to these challenges are the subject of intensive on-going research.

Electric energy was cheap and plentiful in the early years of the industry, but after the rise in oil prices in the early 1970s energy consumption became a major concern. In recent years, carbon dioxide emissions have become a central issue for the industry. Carbon dioxide gas is formed at the anode, as the carbon anode is consumed upon reaction of carbon with the oxygen ions from the alumina (Al_2O_3). Formation of carbon dioxide is unavoidable as long as carbon anodes are used, and it is of great concern because CO_2 is a greenhouse gas. Over the last two decades, concerted action has been taken by the aluminum industry to reduce carbon dioxide emissions, both from the anodes and from energy sources used to generate the electricity required for production. Some aluminum producers are actively engaged in research and development work to try

to minimize or even eliminate the carbon dioxide emissions from the process.

On the other hand there is the great potential for aluminum products, through their production, use, and value recovery (recycling), to reduce both resource use and environmental impact and to increase human well-being and economic activity, and thus to increase the potential for both resource and impact decoupling. The potential for reduction of anthropogenic greenhouse gas emissions through the use of aluminum-intensive, efficient machinery in industry; efficient cabling, turbines, solar panels, consumer durables, and intelligent control systems in energy supply networks; lightweight vehicles; green buildings and protective aluminum packaging that preserves agricultural outputs actually has far greater potential for achieving sustainability than improvements in energy efficiency within the aluminum smelting processes.

Aluminum is also essential in environmental management. Aluminum salts such as potassium aluminum sulfate (alum) are often used for flocculation during the water purification process (mainly surface water). This treatment lowers concentrations of organic materials in the water, reduces the presence of microorganisms (viruses, bacteria, and parasites) that can cause infectious diseases, and improves water color and turbidity.

At present the economic situation for the aluminum industry, like that for many other commodities, is difficult. Nevertheless, as seen in similar scenarios in past decades, demand will catch up with production. Global demand for primary aluminum is estimated to reach 70 million metric tonnes per year by 2020, a doubling since 2010. Modern society continues to create opportunities for use of aluminum, and the overall need for this metal will reflect this trend.